# Supporting Information

## Closing the Loop: Polyimine Thermosets from Furfural Derived Bioresources

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## 1. Synthesis, characterization and stability of OBMF

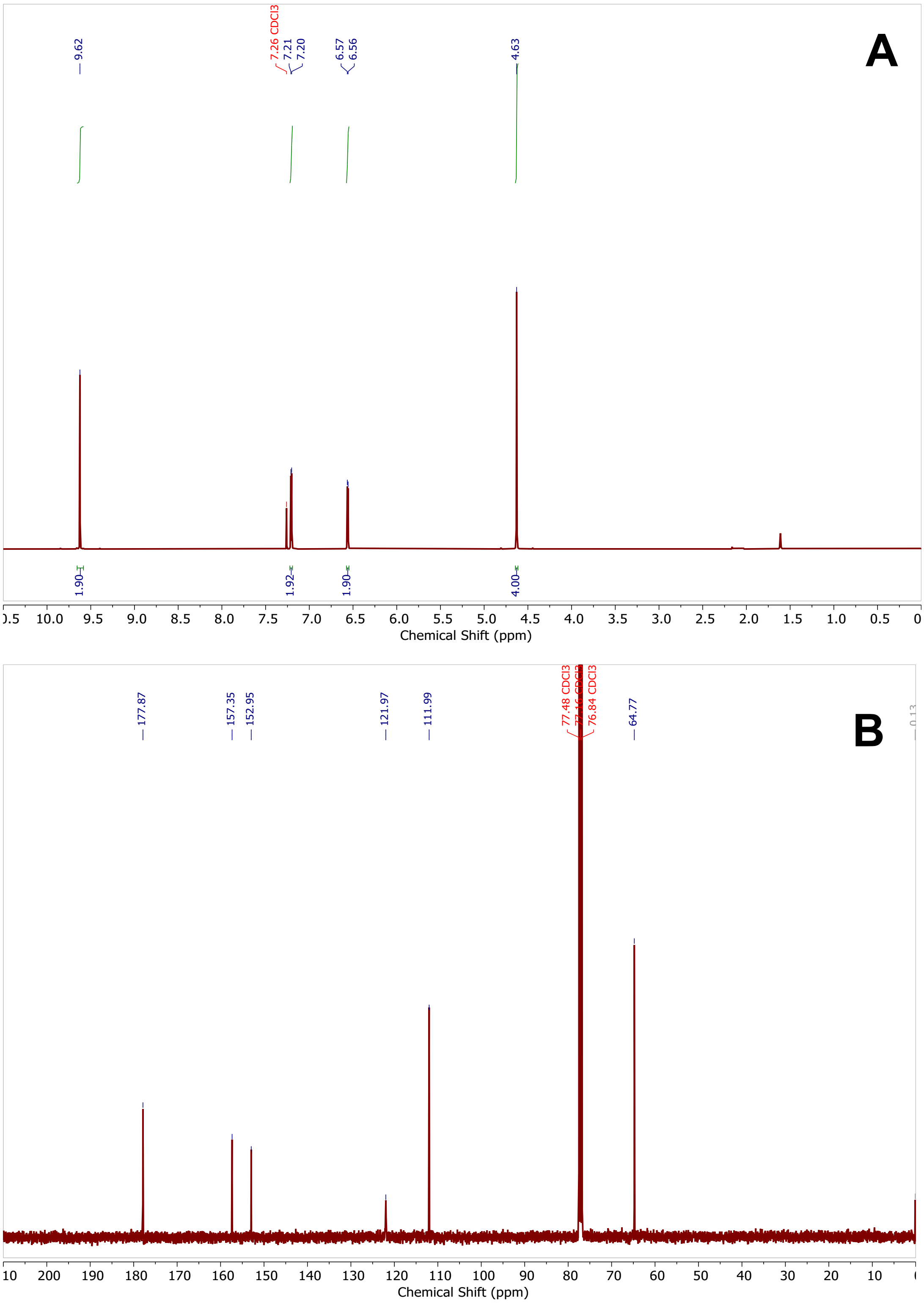
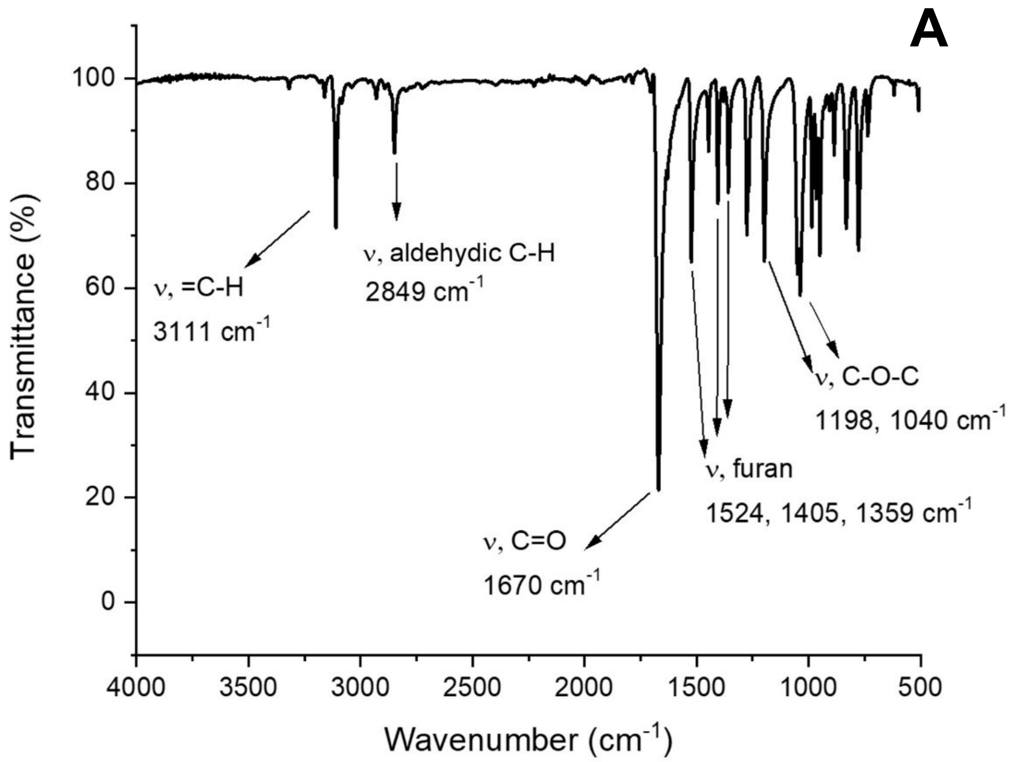



Figure S1. $^{1}H$ NMR (A) and $^{13}C$ NMR (B) spectra of OBMF recorded in $CDCl_3$.



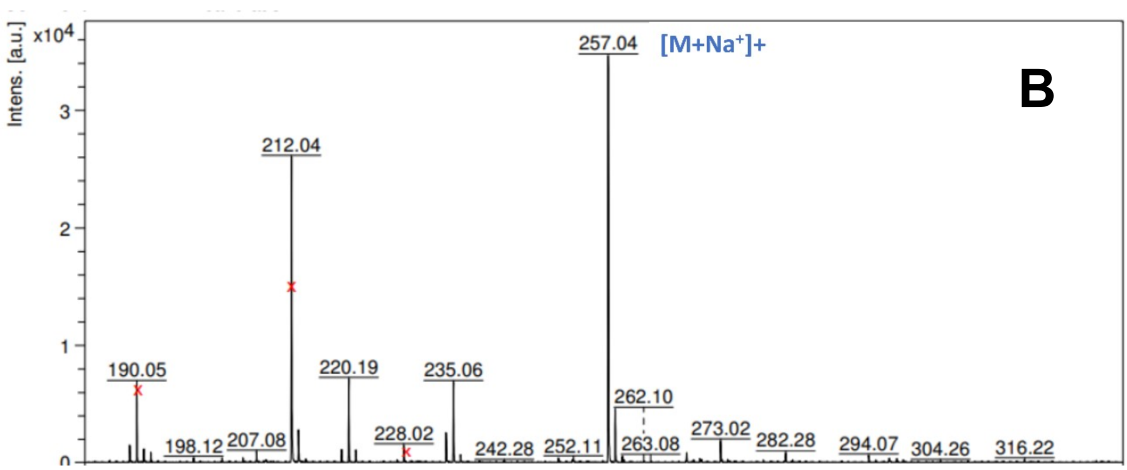




Figure S2. FTIR (A) and MALDI-TOF (B) spectra of OBMF. α-Cyano-4-hydroxycinnamic acid (CHCA) was used as matrix in MALDI measurement. The peaks assigned with x corresponds to the matrix peaks.

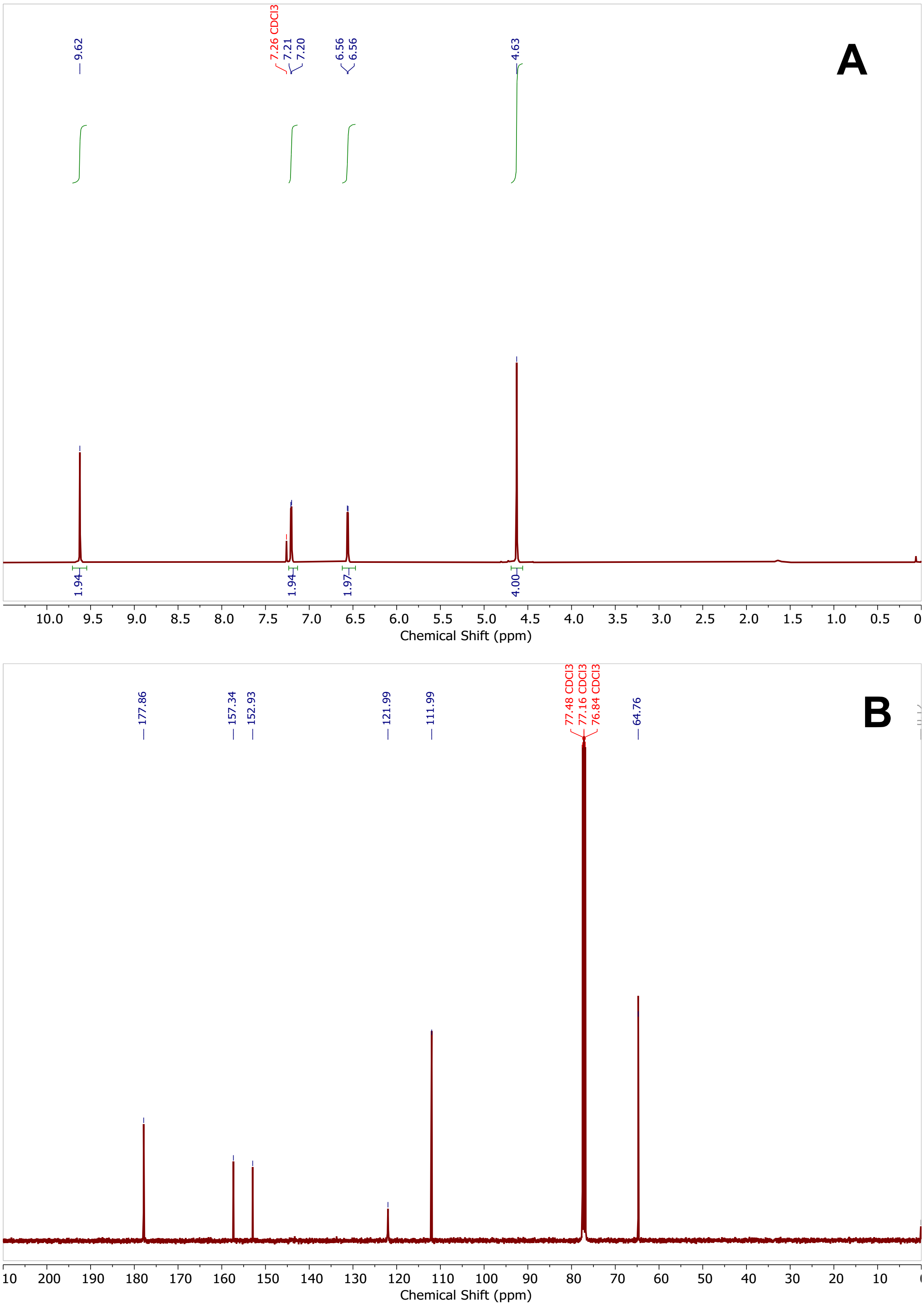



Figure S3. $^{1}H$ NMR (A) and $^{13}C$ NMR (B) spectra of OBMF recorded in $CDCl_3$, after keeping the solids 1-year under ambient conditions.

Table S1. Isolated yields of OBMF at different concentrations of HMF.

| | **Concentration of HMF (mol/L)** | **Isolated Yield (%)** |
|---|---|---|
| **Entry 1** | 0.4 | 64 |
| **Entry 2** | 0.2 | 67 |
| **Entry 3** | 0.1 | 79 |

## 2. Synthesis and structural characterization of the polyimine networks

Table S2. Recipes for the preparation of polyimine networks.

| | **OBMF** | **Diamine** | **Triamine** |
|---|---|---|---|
| **P(FIm)-TREN** | 6 mmol | 0 | TREN 4 mmol |
| **CFRP(FIm)-TREN** | 7.8 mmol | 0 | TREN 5.2 mmol |
| **P(FIm)-PD** | 6 mmol | PD 3 mmol | TREN 2 mmol |
| **P(FIm)-MD** | 6 mmol | MD 3 mmol | TREN 2 mmol |
| **P(FIm)-FD** | 6 mmol | FD 3 mmol | TREN 2 mmol |
| **P(FIm)-Pri** | 6 mmol | Pri 3 mmol | TREN 2 mmol |

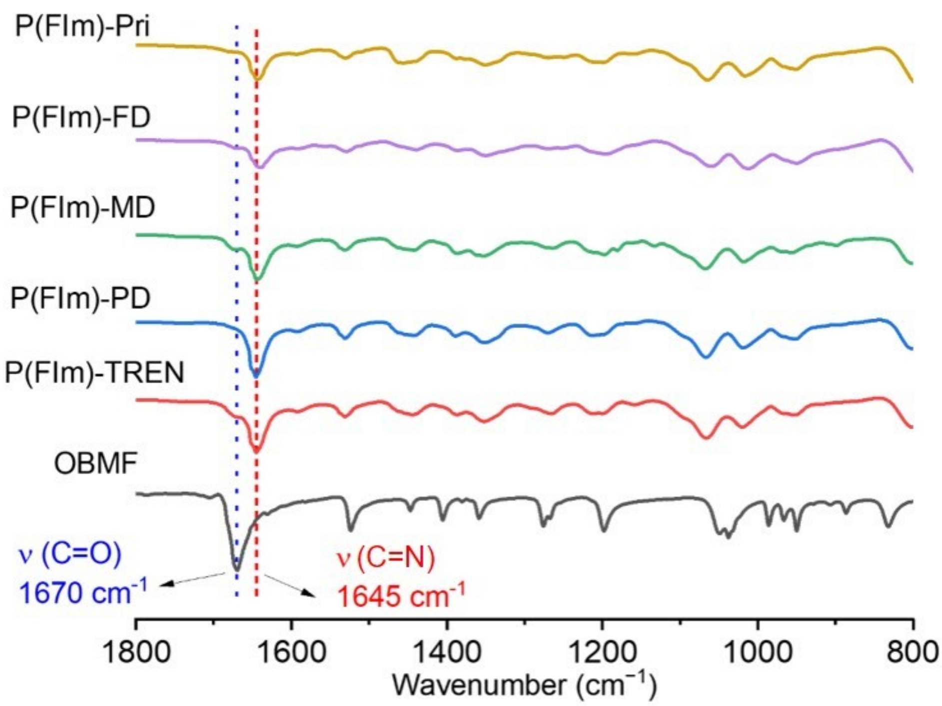



Figure S4. Characterization of the polyimine networks by FTIR.

## 3. Stability of polyimine networks in organic solvents and water

Table S3. Swelling measurements of **P(FIm)-TREN** in different solvents at room temperature.

| Solvents | MeOH | EtOH | Acetone | IPA | THF | n-hexane | $H_2O$ |
|---|---|---|---|---|---|---|---|
| Swelling ratio (%) | 82.6 | 49.2 | 16.2 | 0.8 | 22.5 | 0 | 37.6 |
| Gel content (%) | 88.1 | 95.9 | 99.8 | 99.2 | 99.7 | 98.3 | 98.3 |

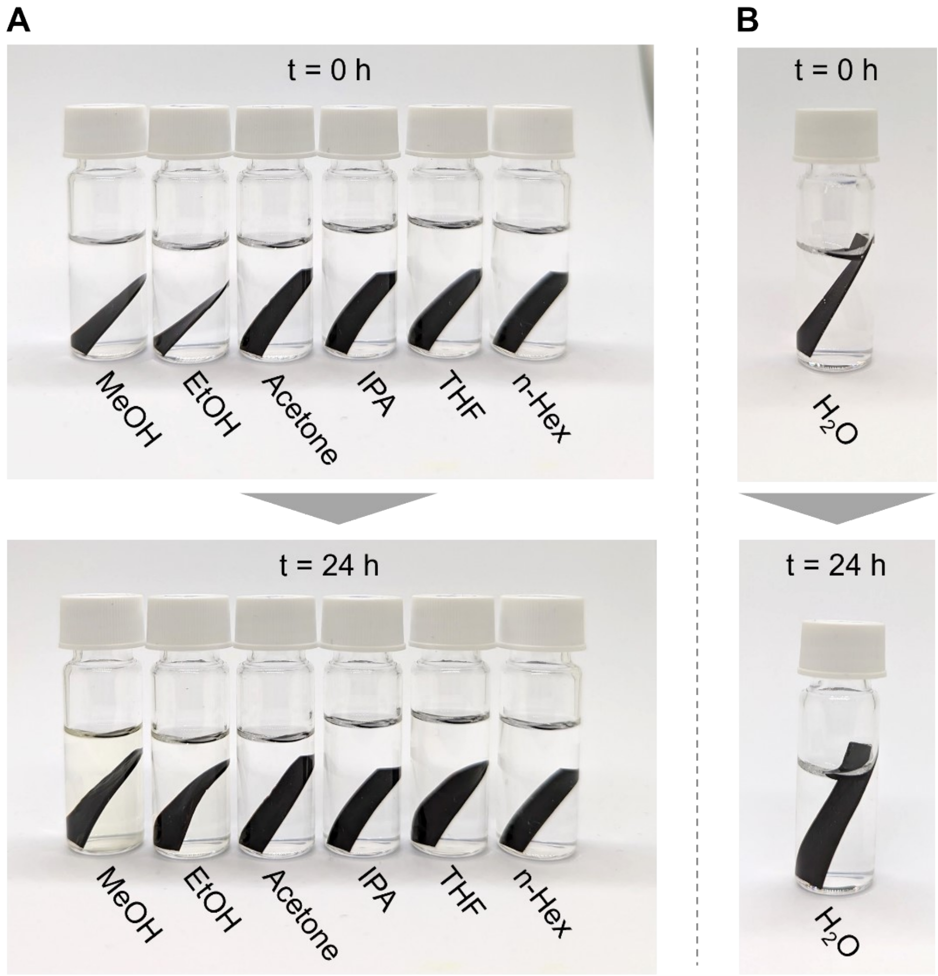



Figure S5. Photographs depicting the solvent resistance of **P(FIm)-TREN** in various organic solvents (A) and water (B) at different time intervals.

Table S4. Swelling measurements of **P(FIm)-FD** in different solvents at room temperature.

| Solvents | MeOH | EtOH | Acetone | IPA | THF | n-hexane | $H_2O$ |
|---|---|---|---|---|---|---|---|
| Swelling ratio (%) | 19.2 | 0.6 | 0.17 | 3.7 | 0.5 | 0.6 | 18.4 |
| Gel content (%) | 95.2 | 99.6 | 99.3 | 99.4 | 99.8 | 99.6 | 97.3 |

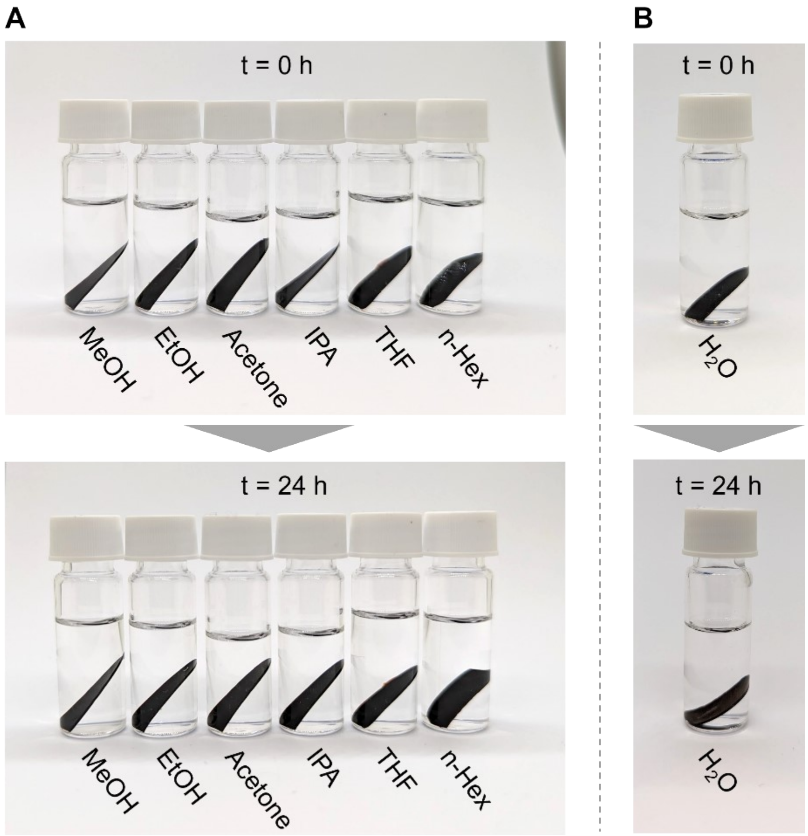



Figure S6. Photographs depicting the solvent resistance of **P(FIm)-FD** in various organic solvents (A) and water (B) at different time intervals.

# 4. Thermal analysis of polyimine networks

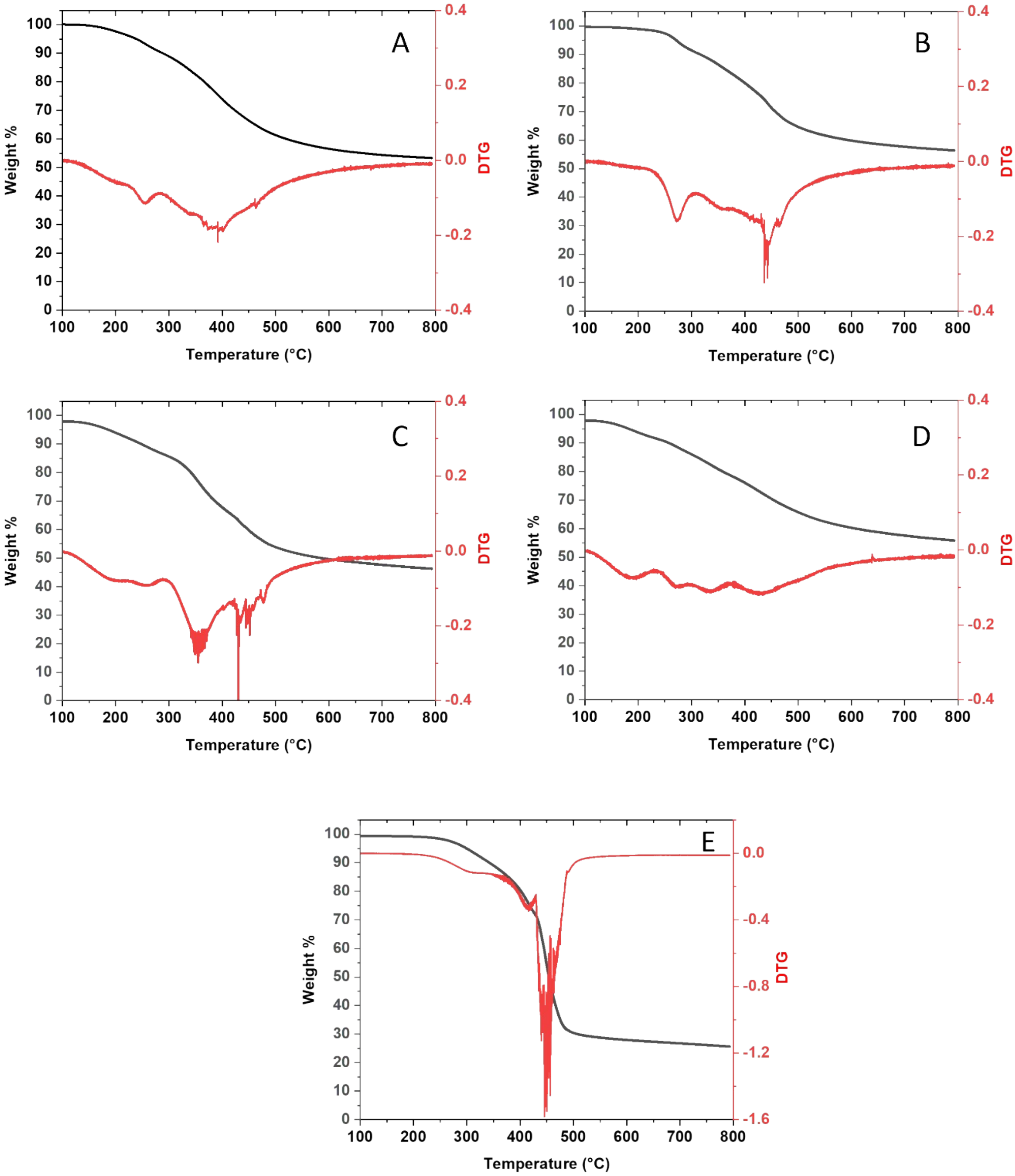



Figure S7. Thermogravimetric analysis (TGA) of the polyimines, performed under $N_2$: **P(FIm)-TREN** (A), **P(FIm)-PD** (B), **P(FIm)-pMD** (C), **P(FIm)-FD** (D), **P(FIm)-Pri** (E).

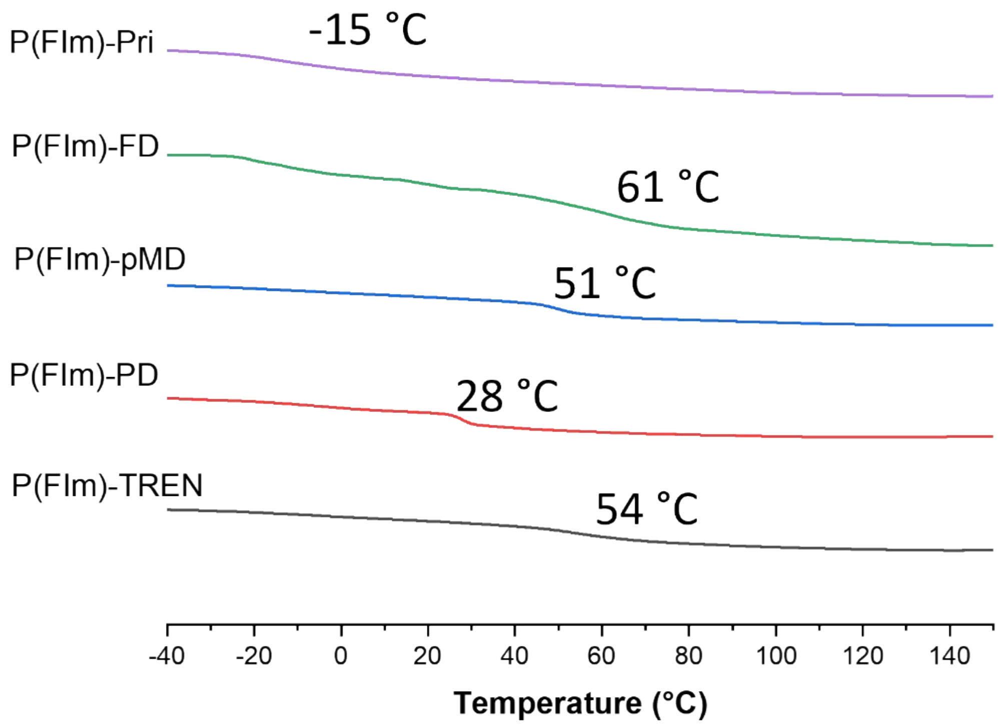



Figure S8. Differential scanning calorimetry (DSC) of the polyimines, performed under $N_2$. The heating rate of P(FIm)-FD and P(FIm)-TREN was 20 °C/min, whereas that of the others was 10 °C/min.

## 5. Thermomechanical analysis of polyimine networks

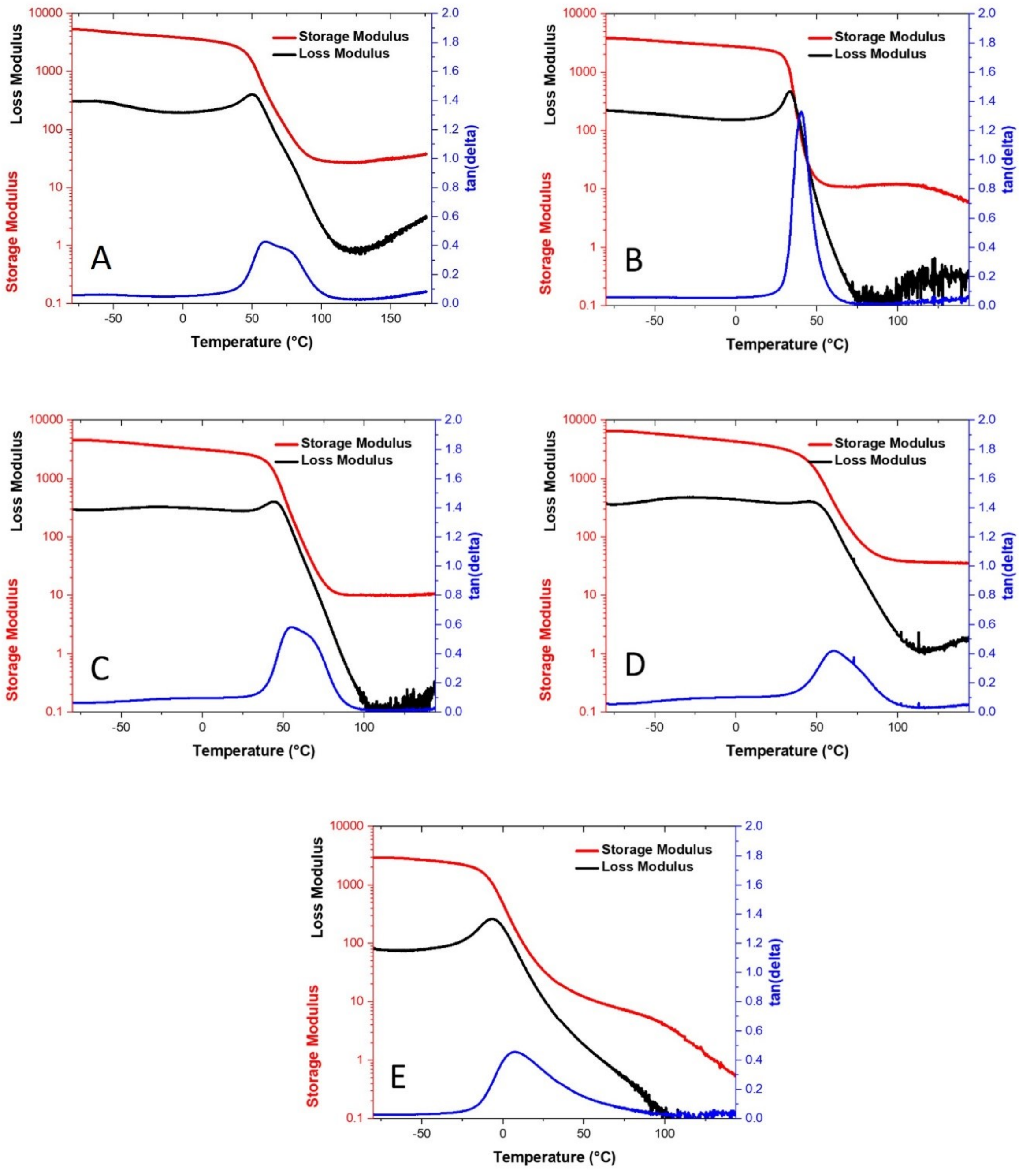
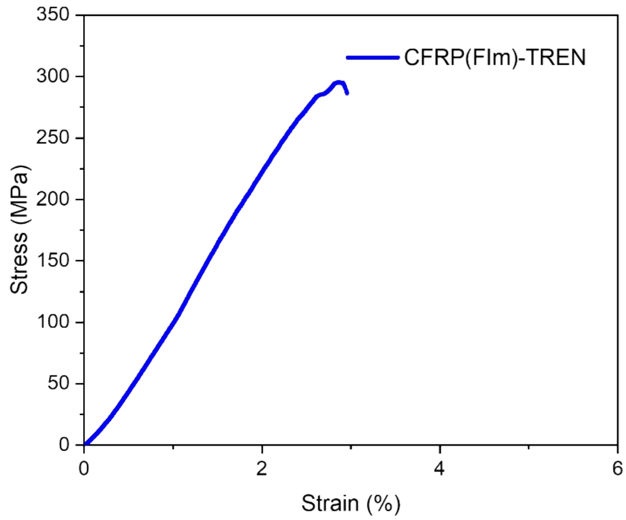



Figure S9. Dynamic mechanical analysis (DMA) of the polyimines: **P(FIm)-TREN** (A), **P(FIm)-PD** (B), **P(FIm)-*p*MD** (C), **P(FIm)-FD** (D), **P(FIm)-Pri** (E).

## 6. Mechanical analysis




| | Maximum stress (MPa) | Strain at break (%) | Young's modulus (GPa) |
|---|---|---|---|
| **CFRP(FIm)-TREN** | 295.1 ± 46.5 | 3.0 ± 0.8 | 10.7 ± 0.9 |

Figure S10. Tensile stress-strain curve of the polyimine based carbon-fiber composite, **CFRP(FIm)-TREN**.

## 7. Scanning electron microscopy

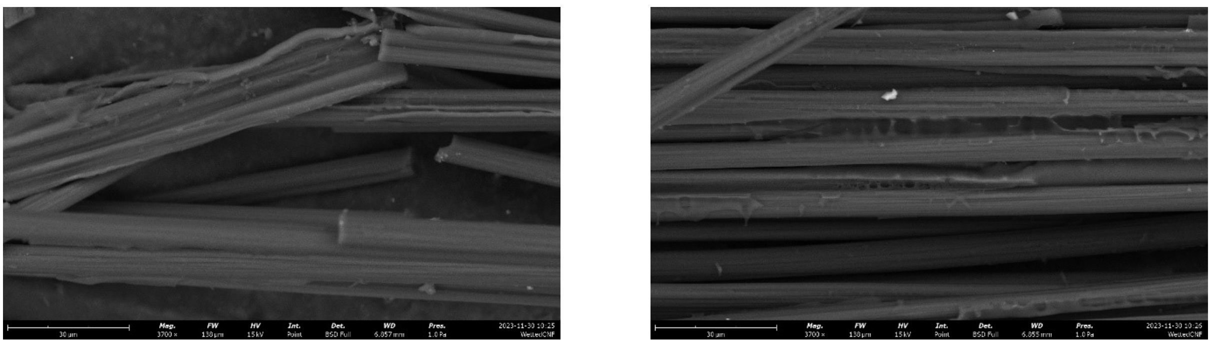


Figure S11. Investigation of the fractured **CFRP(FIm)-TREN** composite by scanning electron microscopy. Scale bar is 30 µm.

## 8. Chemical recycling of the P(FIm)-TREN network

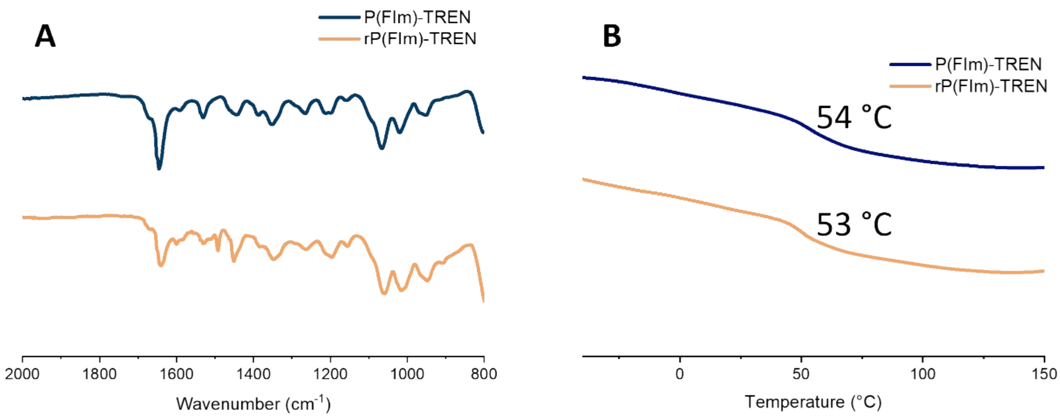



Figure S12. Comparison of the virgin **P(FIm)-TREN** and recycled **rP(FIm)-TREN**: FTIR (A), DSC (B).